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Citation: *The Journal of Chemical Physics* **61**, 5389 (1974); doi: 10.1063/1.1681891View online: <http://dx.doi.org/10.1063/1.1681891>View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/61/12?ver=pdfcov>

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Ab initio study of the $X^2\Pi$ and $A^2\Sigma^+$ states of OH. I. Potential curves and properties

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(Received 21 August 1974)

Accurate *ab initio* CI potential curves and molecular properties are presented for the $X^2\Pi$ and $A^2\Sigma^+$ states of OH. Results with known experimental values in parentheses are $R_e(X^2\Pi) = 1.841(1.834)$ bohr, $R_e(A^2\Sigma^+) = 1.906(1.913)$ bohr, $D_e(X^2\Pi) = 4.43(4.63)$ eV, $D_e(A^2\Sigma^+) = 2.29(2.53)$ eV, $\mu(\text{OH}, X^2\Pi, v=0) = 1.634(1.668)$ D, and $\mu(\text{OH}, A^2\Sigma^+, v=0) = 1.861(1.72 \pm 0.10)$ D. Spectroscopic constants calculated from the theoretical potential curves are in satisfactory agreement with experimental results. Other molecular properties studied include quadrupole moments and the electric field gradient at the nuclei.

I. INTRODUCTION

The hydroxyl radical OH is among the most extensively studied diatomic radicals. Early interest in the spectrum of OH was inspired by its appearance in flames, explosions, and shocks. A knowledge of the structure of the OH bands and the availability of certain band constants are of great importance for temperature measurements, as well as for a general exploration of the physical conditions, in these sources. A detailed analysis of the OH bands in the wavelength region 2800–3500 Å was presented by Dieke and Crosswhite first in a Bumblebee Series Report¹ in 1948, and later in the open literature² in 1962. All of the bands considered by Dieke and Crosswhite belong to one electronic transition, that between the $X^2\Pi$ and the $A^2\Sigma^+$ states. Later spectroscopic studies³ have resulted in refined values for the energy levels and spectroscopic constants. However, the analysis and classification of the band structure presented by Dieke and Crosswhite still remain valid.

Recently, the emission spectrum of OH has been detected both in astrophysical sources and in the atmosphere. This led to a renewed interest in the OH spectrum, focused on electronic, vibrational, and rotational transition probabilities. A knowledge of these transition probabilities is essential for the deduction of internal state populations through emission intensities, as well as for the theoretical determination of rates for a number of important photochemical processes.

In this series of two papers we present accurate, theoretical calculations on the $X^2\Pi$ and $A^2\Sigma^+$ states of OH. Paper I deals with the calculation of the electronic wavefunctions, calculated potential curves, and one-electron properties. Paper II presents calculated dipole transition moments and electronic transition probabilities.

The method used to obtain the potential, one-electron property and electronic transition moment curves has been shown to give accurate results for a number of molecular systems, including CH^+ ,⁴ LiO ,⁵ AlO ,⁵ and CH .⁶ In particular, the calculated transition probabilities appear to be comparable in accuracy to, or even more reliable than, the best available experimental re-

sults. A description of the configuration interaction (CI) method used for the electronic wavefunction calculation is given in Sec. II. Results and discussions are presented in Sec. III.

II. CALCULATIONS

A. Electronic wavefunction

Approximations to the Born–Oppenheimer electronic wavefunctions and energies are calculated using the configuration interaction (CI) method. The wavefunction of a desired electronic state is expanded in an n -particle basis set of orthonormal configuration state functions (CSF). Each CSF is a linear combination of Slater determinants (SD) such that it has the symmetry and multiplicity characteristics possessed by the desired state. The SD's are built from an orthonormal one-particle basis set of symmetry and equivalence restricted spatial orbitals. The spatial orbitals are expanded in terms of a set of symmetry-adapted elementary basis functions. In what follows, we describe the choice of the elementary basis and the construction of the one- and n -particle bases for our calculation on OH.

The elementary basis set, made up of Slater-type functions (STF) centered at the atomic nuclei, is given in Table I. There are six s -, four p -, three d -, and one f functions on the oxygen atom, and four s -, three p -, and two d functions on the hydrogen atom. The sp basis on oxygen is taken from Clementi's SCF calculation on O^+ ,⁷ with one additional diffused $2s$ function, $\zeta = 1.41$. The reason for using a basis set optimized for the negative ion is that both the $X^2\Pi$ and $A^2\Sigma^+$ states of OH have dipole moments in the direction O^-H^+ . Three of the polarization functions on oxygen are chosen such that they are mainly localized in the L shell. These polarization functions are appropriate for describing the distortion of the oxygen atomic orbitals in the molecular field and the change in atomic correlation as a function of internuclear separation. One additional $3d$ function with $\zeta = 1.15$, optimized for the self-consistent-field (SCF) polarizabilities of the oxygen atom, insures the correct long range behavior of the O–H interaction potentials. The

TABLE I. Slater-type basis set of OH.

Center	nl values	Exponents (bohr ⁻¹)
O	1s	13.224, 7.6063
	2s	6.3783, 3.1441, 1.8792, 1.41
	2p	7.907, 3.4379, 1.796, 1.1536
	3d	2.5, 1.15
	4d	2.5
	4f	3.0
H	1s	2.2, 1.0
	2s	2.2, 0.7
	2p	2.6, 1.6, 1.0
	3d	2.7
	4d	2.7

oxygen basis described here reproduces the coupled Hartree-Fock (HF) polarizabilities of oxygen atom to better than 10%. The hydrogen basis is mainly taken from Liu's CI calculation on H_2 and H_3 .⁸ The p functions have been replaced by those used by Green *et al.* in a CI calculation on CH^+ .^{4a} These p functions accurately reproduce the polarizability of the hydrogen atom. One additional change is the replacement of the most diffused 2s function, $\zeta = 1$, by an even more diffused function with $\zeta = 0.7$. This substitution has little effect on calculations on the $X^2\Pi$ and $A^2\Sigma^+$ states of OH, but is essential for calculations on the other valence states of OH which have dipole moments in the direction O^+H^- .⁹ Since the potential curves for these other states are of considerable interest, we felt it desirable to use, for our calculations, a basis set which is suitable for all of the valence states.

The OH basis set described above is very similar to that used by Hinze and Liu in multiconfiguration self-consistent-field (MCSCF) calculations on the valence states of OH.⁹ To obtain some indication of the quality of this basis set, SCF energies have been calculated, with the results $E(X^2\Pi, R=1.795 \text{ bohr}) = -75.42154$ hartree and $E(A^2\Sigma^+, R=1.912 \text{ bohr}) = -75.26624$ hartree. These are to be compared with the previously best SCF energies,¹⁰ at corresponding internuclear distances, of -75.42127 and -75.26553 hartree, respectively. Since this basis set is used in CI calculations, limited optimization of the d - and f functions has been carried out with respect to CI total energies. In all cases examined, the maximum energy improvement is less than 0.001 hartree, with attendant change in the calculated binding energy of less than 0.0005 hartree.

The construction of the one- and n -particle basis sets follows closely the procedure used by Lie, Hinze, and Liu^{8a} in calculations on the valence states of CH. This procedure begins with a MCSCF calculation, involving a small number of CSF's, chosen to give a qualitatively correct potential curve for the range of internuclear distances under consideration. The first order Rayleigh-Schrödinger perturbation theory is used, with this MCSCF wavefunction as a zeroth order wavefunction, to select classes of CSF's that form the n -particle basis for an extended CI calculation. In this CI calculation, the CSF's are constructed from approximate natural orbitals (NO) obtained also with the aid of perturbation theory. The use of these NO's permits a severe truncation of the one-particle basis, and consequently a

very significant reduction of the dimension of the n -particle space, with only small loss to the calculated energies. Details of this procedure are given below.

The one-particle space is partitioned into three subspaces: the core space, the internal space, and the external space. The core space contains a single orbital, 1σ , which correlates with the $1s$ orbital of the oxygen atom. The internal space is spanned by three σ - and one π orbitals, 2σ , 3σ , 4σ , and 1π , which correlate with the $2s$ and $2p$ orbitals of oxygen atom and the $1s$ orbital of hydrogen. The external space is the remainder of the one-particle space spanned by the one-particle basis set. The core and internal orbitals are determined by MCSCF calculations on a small number of CSF's:

$$\begin{aligned}
 X^2\Pi \quad & 1\sigma^2 2\sigma^2 3\sigma^2 1\pi^3 \\
 & 1\sigma^2 2\sigma^2 4\sigma^2 1\pi^3 \\
 & 1\sigma^2 2\sigma^2 (3\sigma 4\sigma, {}^3\Sigma^+) 1\pi^3
 \end{aligned}$$

and

$$\begin{aligned}
 A^2\Sigma^+ \quad & 1\sigma^2 2\sigma^2 3\sigma 1\pi^4 \\
 & 1\sigma^2 2\sigma^2 3\sigma 4\sigma^2 1\pi^2 \\
 & 1\sigma^2 3\sigma 4\sigma^2 1\pi^4 \\
 & 1\sigma^2 3\sigma^2 4\sigma 1\pi^4 \\
 & 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 1\pi^2.
 \end{aligned}$$

The first CSF in each of these lists is the Hartree-Fock CSF. The other CSF's are necessary for proper descriptions of the separated atom limits and for qualitatively correct potential curves for all internuclear distances. These CSF's, called reference CSF's, play an important role in selecting CSF's for the extended CI calculation.

The n -particle basis for the extended CI calculation includes only CSF's with a doubly occupied 1σ orbital. This neglect of all correlation effects connected with the 1σ electrons is reasonable, because they remain essentially unchanged during molecular formation. Three types of CSF's are included in the n -particle basis:

(a) valence CSF's—all CSF's arising from distributing seven valence electrons among the four internal orbitals;

(b) all CSF's arising from distributing six valence electrons in the internal orbitals and one electron in external orbitals;

(c) All CSF's arising from distributing five valence electrons in the internal orbitals and two in the external orbitals, with the additional constraint that only CSF's that have nonzero Hamiltonian matrix elements with at least one of the reference CSF's are allowed.

These three types together include all CSF's that appear in the first order Rayleigh-Schrödinger perturbation wavefunction, if the zeroth order wavefunction is constructed from the "reference CSF's." A detailed discussion of CSF selection based on perturbation theory has been given by McLean and Liu.¹¹

The actual calculation for each point on the potential

curves of OH is carried out in four steps:

- (1) an MCSCF calculation on the reference CSF's;
- (2) a CI calculation including all CSF's of type (a), constructed from the MCSCF occupied orbitals;
- (3) a first-order Rayleigh-Schrödinger perturbation calculation using the CI wavefunction obtained in step (2) as the zeroth order approximation. The first-order wavefunction is expanded in an n -particle basis set which includes all CSF's of type (c) that can be constructed from the full set of MCSCF occupied and virtual orbitals. This is followed by the extraction of NO's from the resultant wavefunction, the sum of the zeroth and the first-order wavefunctions;
- (4) the NO's obtained in step (3) are ordered by symmetry and decreasing occupation numbers and truncated to 12σ -, 9π -, 6δ -, and 1ϕ -type orbitals. The final CI calculation includes all CSF's of types (a), (b), and (c) that can be constructed from this truncated one-particle basis.

The n -particle basis sets for the final CI calculations contain 7311 and 3965 CSF's for the $X^2\Pi$ and $A^2\Sigma^+$ states, respectively.

The CI wavefunctions are used to calculate expectation values for a number of one-electron operators and the dipole transition moment between the $X^2\Pi$ and $A^2\Sigma^+$ states.

The MCSCF calculations described here were performed using a computer program developed by J. Hinze. All other calculations were performed using *ALCHEMY*, a system of programs for the calculation of molecular wavefunctions developed by P. S. Bagus, B. Liu, A. D. McLean, and M. Yoshimine.

B. Nuclear wavefunction and spectroscopic constants

In the Born-Oppenheimer approximation, the total wavefunction of a diatomic molecule is written as a product of electronic and nuclear wavefunctions. The nuclear wavefunction is a solution of the Schrödinger equation for nuclear motions, in which the electronic energy as a function of R appears as the potential energy operator. For a diatomic molecule, a further assumption of separability of the radial and angular dependence of the nuclear wavefunction permits the explicit solution of the rotational eigenvalue problem and leaves a radial Schrödinger equation for nuclear vibration, which contains both the electronic and rotational eigenenergies as potential energy operators. The eigenvalues of this equation, E_{vN} , give the energy levels of the diatomic molecule. The vibrational quantum number has values

$$v = 0, 1, 2, \dots$$

and the rotational quantum number has values

$$N = \Lambda, \Lambda + 1, \Lambda + 2,$$

where Λ is the electronic angular momentum along the internuclear axis. Here we have adopted the notations of Hund's coupling case b. While this is appropriate for the $A^2\Sigma^+$ state, it should be noted that the $X^2\Pi$ state of OH is intermediate between coupling cases a and b. However, in this work we have neglected all interactions

with electronic spin, in which case the solutions to the radial Schrödinger equation is, for all practical purposes, unaffected by the assumption of coupling cases.

The energy levels $E_{v,N}$ can be expressed as

$$E_{v,N} = G_v + B_v[N(N+1) - \Lambda^2] - D_v N^2(N+1)^2 + \dots \quad (1)$$

The spectroscopic constants G_v , B_v , and D_v can be determined by a least square fit procedure, using calculated E_{vN} . Experience shows that the values of these constants depend little on the number of rotational levels used in the least square fit. These constants, as functions of v , can again be expanded as

$$G_v = T_e + \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \dots \quad (2)$$

and

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \dots \quad (3)$$

The spectroscopic constants ω_e , $\omega_e x_e$, B_e , and α_e can again be obtained by a least square fit. However, in these cases, the spectroscopic constants vary significantly with the number of vibrational levels used in the least square fit. In this work, care has been taken to use the same number of vibrational levels for obtaining these spectroscopic constants, as in their experimental determination. This is the only way to achieve a meaningful comparison between theory and experiment.

The vibrational wavefunctions described above are obtained by numerical integration of the radial Schrödinger equation. These wavefunctions are used to obtain vibrational averages for a number of observable properties. The computer program used for these calculations were developed by K. Docken and J. Hinze and modified by B. Liu.

III. RESULTS AND DISCUSSION

A. Potential curves and spectroscopic constants

The calculated MCSCF and CI potential curves for the $X^2\Pi$ and $A^2\Sigma^+$ state of OH are presented in Table II. The CI potential curves are also shown in Fig. 1.

Five points around the computed energy minimum of each CI potential curve were fitted to a cubic polynomial using the least square method. The resulting analytical formulas were used to determine the equilibrium internuclear separations and the potential minima. Table III gives the calculated potential minimum E_{\min} , equilibrium internuclear separation R_e , dissociation energy D_e , term energy T_e , and term energy at the separated-atom limit. Experimental values are given in parenthesis for comparison.

The calculated R_e differ from experimental results by 0.007 bohr. Calculations on CH^{6a} and HF,¹² using the same CI procedure, have yielded R_e within 0.002 and 0.005 bohr, respectively, of known experimental results. It seems safe to assume that the CI procedure adopted for these calculations are capable of predicting equilibrium internuclear distances for the valence state of the hydrides of first row atoms to within 0.01 bohr.

TABLE II. Calculated potential curves for the $X^2\Pi$ and $A^2\Sigma^+$ states of OH. R given in bohrs and energies in hartrees.

R	$E(X^2\Pi)$		$E(A^2\Sigma^+)$	
	MCSCF	CI	MCSCF	CI
1.00	-75.831658	-75.027043	-74.641230	-74.847524
1.20	-75.195170	-75.392155	-75.011299	-75.218293
1.30	-75.294513	-75.489988	-75.112239	-75.319735
1.50	-75.400971	-75.595770	-75.222694	-75.431431
1.70	-75.439038	-75.633306	-75.264684	-75.474700
1.80	-75.444117	-75.637792	-75.271778	-75.482671
1.85	-75.444421	-75.638313	-75.273112	-75.484445
1.90	-75.443573	-75.637323	-75.273311	-75.485056
1.95	-75.441779	-75.635369	-75.272585	-75.484728
2.00	-75.439214	-75.632620	-75.271114	-75.483602
2.20	-75.423943	-75.616311	-75.260746	-75.474125
2.50	-75.395420	-75.585193	-75.244315	-75.453666
2.70	-75.377130	-75.564470	-75.236696	-75.439777
3.00	-75.354024	-75.536998	-75.230744	-75.422990
3.50	-75.329135	-75.504687	-75.229052	-75.408117
4.00	-75.317642	-75.487874	-75.230127	-75.403268
5.00	-75.311362	-75.477530	-75.231629	-75.401304
6.00	-75.310420	-75.475676	-75.231993	-75.401004
8.00	-75.310246	-75.475545	-75.232064	-75.400997
10.00	-75.310241	-75.475452	-75.232065	-75.400886
15.00	-75.310241	-75.475430	-75.232064	-75.400840
20.00	-75.310241	-75.475432	-75.232064	-75.400835

These comparisons suggest that the *exceedingly* good agreement between the calculated and experimental R_e obtained for CH is possibly fortuitous.

The calculated dissociation energies are in error by 0.20 and 0.24 eV for the $X^2\Pi$ and $A^2\Sigma^+$ states, respectively. The fact that these errors are somewhat larger than those obtained for CH^{6a} can probably be attributed to the smaller one-particle basis set used in this calculation. Similar calculation on HF¹² with untruncated

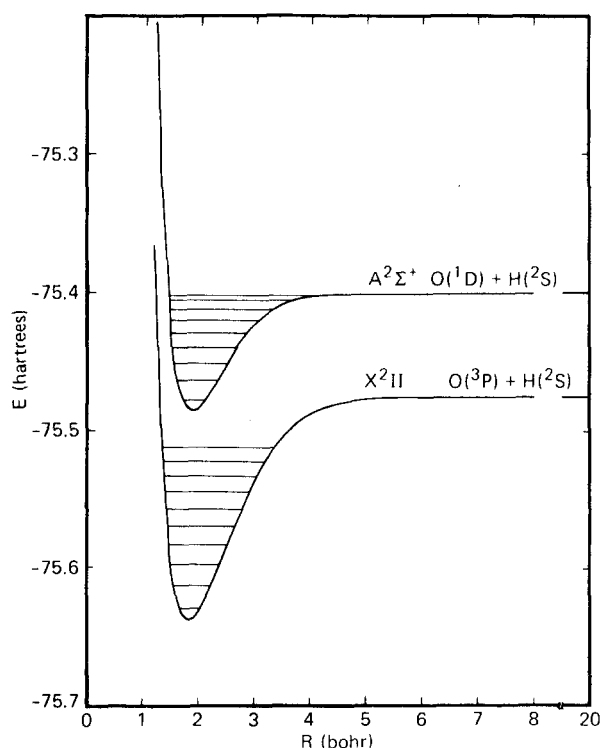
FIG. 1. Extended CI potential curves for the $X^2\Pi$ and $A^2\Sigma^+$ states of OH.

TABLE III. Properties of the calculated potential curves. Experimental values are given in parentheses.

State	E_{\min} (hartree)	R_e (bohr)	D_e (eV) ^a	T_e (cm ⁻¹)	T_0 (cm ⁻¹)
$X^2\Pi$	-75.63832	1.841 (1.834) ^b	4.43 (4.63) ^c		
$A^2\Sigma^+$	-75.48507	1.906 (1.913) ^b	2.29 (2.53) ^d	33618 (32682.5) ^b	16372.1 (15867.7) ^e

^aObtained from experimental D_0 values and the RKR zero point energies obtained by R. J. Fallon, I. Tobias, and J. T. Vanderslice, J. Chem. Phys. **34**, 167 (1961).

^bTaken from G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950).

^c D_0 value taken from P. G. Williamson's compilation [Astrophys. J. **138**, 788 (1963), Table I, plus annotations]. This value differs from that given in Ref. b, which corresponds to $D_e = 4.58$ eV.

^d D_0 value given by C. Carlone and F. W. Dalby, Can. J. Phys. **47**, 1945 (1969). This value is consistent with $D_e(X^2\Pi) = 4.63$ eV. Data given in Ref. b lead to $D_e(A^2\Sigma^+) = 2.49$ eV.

^eC. E. Moore, "Atomic Energy Levels," Natl. Bur. Stand. Circ. 467, (1949).

one-particle basis set yielded dissociation energy within 0.08 eV of the experimental value.

Calculated term energy for the $A^2\Sigma^+$ state is 33618 cm⁻¹, as compared to the experimental result of 32682.5 cm⁻¹. This result is in error by 1035 cm⁻¹. Nearly half of this error can be attributed to the calculated term splitting of the ¹D and ³P states of oxygen, which is in error by 504 cm⁻¹.

Calculated vibrational quanta, $\Delta G_{v+1/2} = G_{v+1} - G_v$, and rotational constants B_v and D_v , for OH and OD are presented in Tables IV and V, respectively. Calculated vibrational constants ω_e , $\omega_e x_e$, B_e , and α_e are given in Table VI. Also given in Table VI are calculated zero point vibrational energy, dissociation energy D_0 , and term energy ν_{00} . Available experimental values are given in parentheses for comparison.

The calculated $\Delta G_{v+1/2}$ are in reasonable agreement with experimental results. In general, the difference between calculated and experimental results increases

TABLE IV. Rotational constants of OH. All energy quantities are given in cm⁻¹. Experimental values are given in parentheses.

State	V	$\Delta G_{v+1/2}$ ^a	B_v ^b	$D_v \times 10^3$ ^b
$X^2\Pi$	0	3547(3570)	18.55(18.547)	1.94(1.9003)
	1	3380(3404)	17.86(17.838)	1.90(1.8692)
	2	3225(3240)	17.12(17.136)	1.82(1.837)
	3	3054(3077)	16.39	1.84
	4	2882(2916)	15.71	1.85
	5	2714(2751)	15.00	
$A^2\Sigma^+$	0	2986(2989)	17.04(16.960)	2.08(2.039)
	1	2774(2793)	16.15(16.126)	2.09(2.024)
	2	2572(2593)	15.29(15.284)	2.07(2.027)
	3	2350(2386)	14.40(14.423)	2.13(2.067)
	4	2079	13.41	2.35

^aExperimental values taken from R. J. Fallon, I. Tobias, and J. T. Vanderslice, J. Chem. Phys. **34**, 167 (1961).

^bExperimental values taken from E. A. Moore and W. G. Richards, Phys. Scr. **3**, 223 (1971).

TABLE V. Rotational constants of OD. All energy quantities are given in cm^{-1} . Experimental values are given in parentheses.

State	V	$\Delta G_{v+1/2}$	B_v	$D_v \times 10^{-3}$
$X^2\Pi$	0	2612(2632) ^a	9.88(9.87) ^c	0.55(0.42) ^c
	1	2524(2544) ^a	9.63(9.57) ^c	0.54(0.36) ^c
	2	2450(2455) ^a	9.33(9.28) ^c	0.51
	3	2355	9.05	0.53
	4	2262	8.79	0.53
	5	2178	8.51	0.50
	6	2090	8.23	0.50
$A^2\Sigma^+$	0	2218(2214.6) ^b	9.10(9.037) ^b	0.59(0.55) ^b
	1	2100(2111.5) ^b	8.75(8.714) ^b	0.59(0.54) ^b
	2	1994(2007.5) ^b	8.42(8.393) ^b	0.58(0.55) ^b
	3	1887	8.08(8.068) ^b	0.58(0.55) ^b
	4	1774	7.75	0.59
	5	1643	7.38	0.63

^aM. A. A. Clyne, J. A. Coxon, and A. R. Woon Fat, *J. Mol. Spectrosc.* **46**, 146 (1973).

^bC. Carlone and F. W. Dalby, *Can. J. Phys.* **47**, 1945 (1969).

^cObtained from spectroscopic constants given in G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950).

with increasing v . For the $X^2\Pi$ state of OH, the calculated $\Delta G_{1/2}$ is in error by 23 cm^{-1} , whereas $\Delta G_{11/2}$ is in error by 37 cm^{-1} . Similarly, for the $A^2\Sigma^+$ state of OH, the calculated $\Delta G_{1/2}$ is only in error by 3 cm^{-1} and $\Delta G_{7/2}$ by 36 cm^{-1} .

The calculated B_v are all within 0.1 cm^{-1} of the known

TABLE VI. Equilibrium spectroscopic constants for OH and OD. Experimental values are given in parentheses.

	OH		OD	
	$X^2\Pi$	$A^2\Sigma^+$	$X^2\Pi$	$A^2\Sigma^+$
$\omega_e(\text{cm}^{-1})$	3713.0 (3735.21) ^a	3198.5 (3184.28) ^a	2701.0 (2720.9) ^b	2336.1 (2319.9) ^b
$\omega_e x_e(\text{cm}^{-1})$	83.2 (82.81) ^a	106.2 (97.84) ^a	44.3 (44.2) ^b	59.0 (52.0) ^b
$B_e(\text{cm}^{-1})$	18.87 (18.871) ^a	17.50 (17.355) ^a	9.99 (10.01) ^b	9.27 (9.19) ^b
$\alpha_e(\text{cm}^{-1})$	0.68 (0.714) ^a	0.88 (0.807) ^a	0.25 (0.29) ^b	0.35 (0.32) ^b
Zero point energy (cm^{-1})	1847 (1848) ^c	1578 (1566) ^c	1352 (1344) ^d	1155 (1150) ^d
$D_0(\text{eV})$	4.20 (4.40) ^e	2.10 (2.34) ^f	4.26 (4.46) ^g	2.15 (2.39) ^f
$\nu_{00}(\text{cm}^{-1})$		33349 (32402.1) ^b		33421 (32490) ^b

^aG. H. Dieke and H. M. Crosswhite, *J. Quant. Spectrosc. Radiat. Transfer* **2**, 97 (1961).

^bG. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950).

^cRKR results given by R. J. Fallon, I. Tobias, and J. T. Vanderslice, *J. Chem. Phys.* **34**, 167 (1961).

^dObtained from the zero point energies of OH and the difference between the zero point energies of OH and OD given by C. Carlone and F. W. Dalby, *Can. J. Phys.* **47**, 1945 (1969).

^eTaken from P. G. Wilkinson's compilation [*Astrophys. J.* **138**, 778 (1963), Table I, plus annotation].

^fC. Carlone and F. W. Dalby, *Can. J. Phys.* **47**, 1945 (1969).

^gObtained from $D_0(\text{OH})$ and the zero point energies of OH and OD.

^hObtained from experimental T_e (see Table III) and zero point energies.

TABLE VII. Comparison of calculations on the $X^2\Pi$ state of OH.

	$R_e(\text{bohr})$	$D_e(\text{eV})$	$\omega_e(\text{cm}^{-1})$	$\omega_e x_e(\text{cm}^{-1})$	$B_e(\text{cm}^{-1})$	$\alpha_e(\text{cm}^{-1})$
Extended CI ^a	1.841	4.43	3713.0	83.2	18.87	0.68
First order ^b wavefunction	1.795	4.26	3675		18.7	
OVC ^c	1.840	4.532	3723.6	-83.15	18.79	0.628
Experimental ^d	1.834	4.63	3735.21	82.81	18.87	0.714

^aThis work.

^bV. Bondybey, P. K. Pearson, and H. F. Schaefer, III, *J. Chem. Phys.* **57**, 1123 (1972).

^cW. J. Stevens, G. Das, A. C. Wahl, M. Krauss, and D. Neumann (unpublished).

^dTaken from Tables IV and VI.

experimental values, and the calculated D_0 are within $1 \times 10^{-4} \text{ cm}^{-1}$ of experimental values.

In deriving the equilibrium spectroscopic constants ω_e and $\omega_e x_e$, we have used only the $v=0$ and $v=1$ vibrational levels, as was done in their experimental determination. This is essential for a meaningful comparison, because these constants vary strongly with the number of vibrational levels used in their derivation. The variation can be as much as 100 cm^{-1} for ω_e and 20 cm^{-1} for $\omega_e x_e$. The variations in the determination of B_e 's and α_e 's are not as drastic. The discrepancies between calculated and experimental quantities are 22 cm^{-1} (1%) or less for ω_e , 10 cm^{-1} (10%) or less for $\omega_e x_e$, 0.15 cm^{-1} (1%) or less for B_e , and 0.08 cm^{-1} (15%) or less for α_e .

The zero point energies given in Table VI are rotationless, i.e., the rotational energies have been subtracted out of the energy of the lowest vibration-rotational level. These rotationless zero point energies are used to determine D_0 and ν_{00} . The calculated zero point energies are all within 12 cm^{-1} (0.8%) of known experimental results. It follows then that the calculated D_0 's and ν_{00} 's have the same accuracy as the calculated D_e 's and T_e 's.

Recent theoretical calculations on OH include the first order wavefunction calculation by Bondybey, Pearson, and Schaefer,¹³ and the optimized valence configuration (OVC) calculation by Stevens *et al.*,¹⁴ both on the $X^2\Pi$ state. Some results from these calculations are given in Table VII for comparison. It is seen that the CI and OVC results are in excellent agreement. OVC gives a somewhat better D_e , while CI results on B_e and α_e are better. The first order wavefunction results are somewhat less accurate.

B. Molecular properties

Table VIII presents calculated dipole moments, μ , quadrupole moments with respect to the center of mass of OH, Q , and electric field gradient at the oxygen and hydrogen nuclei, q_O and q_H , as functions of R . The dipole moment curves are also shown in Fig. 2.

In the calculation of these properties, the molecular axis has been taken as the z axis. Only nonzero components of the dipole vector and the quadrupole moments and electric field gradient tensors are given.

TABLE VIII. Calculated one-electron properties of OH. Dipole moments, μ , given in debyes, quadrupole moments, Q , given in $\text{esu} \cdot \text{cm}^2 \times 10^{-26}$, electric field gradient at the nucleus, in atomic units.

R	$X^2\Pi$					$A^2\Sigma^+$				
	μ	Q	q_O	q_H		μ	Q	q_O	q_H	
1.0000	1.36459	0.70737	-0.69033	8.96414		0.40367	1.99098	4.00194	9.31076	
1.2000	1.44170	0.90053	-0.62390	4.15918		0.65775	2.35880	3.85709	4.38951	
1.3000	1.46900	1.02892	-0.51675	2.87685		0.80357	2.57425	3.88514	3.07495	
1.4000	1.50879	1.15949	-0.38900	2.01016		0.96038	2.80732	3.94857	2.17644	
1.5000	1.54338	1.29709	-0.24577	1.41099		1.12542	3.06053	4.03118	1.55346	
1.6000	1.57497	1.44405	-0.09660	0.99253		1.29681	3.33308	4.12126	1.11595	
1.7000	1.60253	1.59815	0.05314	0.69772		1.47088	3.62332	4.21649	0.80579	
1.8000	1.62534	1.75801	0.20242	0.48857		1.64398	3.92587	4.31876	0.58421	
1.8500	1.63689	1.83965	0.27091	0.40772		1.72899	4.08009	4.37248	0.49795	
1.9000	1.64573	1.92145	0.34101	0.33940		1.81261	4.23571	4.42803	0.42465	
1.9500	1.65363	2.00391	0.40963	0.28166		1.89389	4.39154	4.48508	0.36231	
2.0000	1.65889	2.08517	0.47708	0.23273		1.97267	4.54719	4.54403	0.30928	
2.2000	1.66357	2.40331	0.73150	0.10185		2.24054	5.12775	4.79841	0.16599	
2.5000	1.60536	2.81464	1.06255	0.01657		2.42309	5.72750	5.19595	0.06827	
2.7000	1.51763	3.01183	1.24635	-0.00500		2.36267	5.86138	5.43417	0.03991	
3.0000	1.31830	3.14813	1.46337	-0.01479		1.97813	5.51104	5.59906	0.02144	
3.5000	0.86831	2.91175	1.67284	-0.01028		1.03893	4.03919	5.20580	0.01210	
4.0000	0.45936	2.38425	1.74095	-0.00351		0.45524	2.93397	4.61713	0.00783	
5.0000	0.10209	1.86499	1.74391	0.00052		0.09288	2.35420	4.09223	0.00307	
6.0000	0.02119	1.97398	1.73728	0.00056		0.02635	2.51364	3.98123	0.00141	
8.0000	0.00357	2.77107	1.74453	0.00028		0.00493	3.32297	3.93503	0.00036	

The calculated dipole moments for both states are in the direction ($O^- - H^+$).

The vibrationally averaged dipole moment for the $v=0$ level of the $X^2\Pi$ state is 1.634 D for both OH and OD.

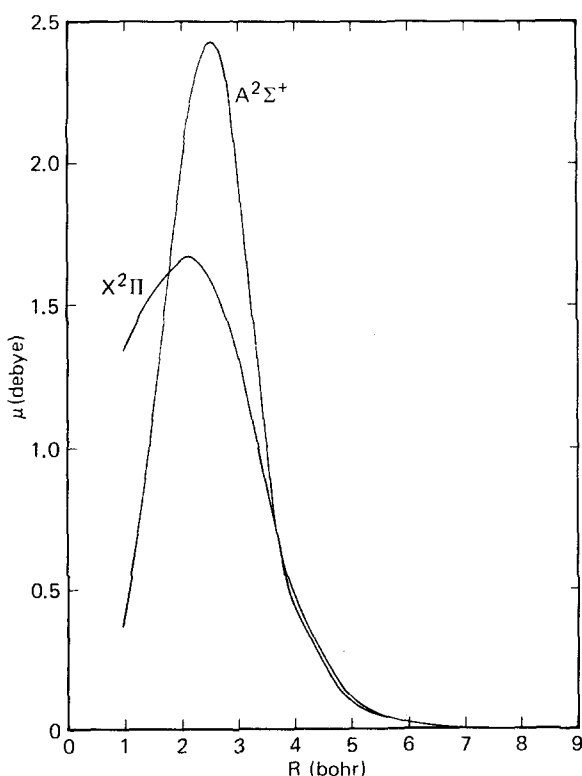


FIG. 2. Extended CI dipole curves for the $X^2\Pi$ and $A^2\Sigma^+$ states of OH.

This is to be compared with the most recent experimental values of $\mu(\text{OH}) = 1.6676(9)$ D and $\mu(\text{OD}) = 1.65312(14)$ D by Meerts and Dymanus¹⁵ and with the OVC results¹⁴ of $\mu(\text{OH}) = 1.68$ D. An error of ~ 0.04 D in our calculated dipole moments is consistent with previous experience in the *ab initio* calculations of dipole moments of diatomic molecules. Our calculated results do not reproduce the experimental isotope effects on the dipole moment. A possible explanation for this discrepancy is that the maximum in the calculated dipole curve (Fig. 2) is too low, and/or occurs at too small an internuclear separation. The OVC dipole curve has a somewhat higher (~ 0.1 D) maximum. We have estimated an upper bound to isotope effect of ~ 0.003 D for this dipole curve, using an R -centroid approximation. Similarly, estimates based on an empirical dipole curve,¹⁶ obtained from vibrational transition data, also failed to produce isotope effects of more than 0.005 D. Thus, assuming the correctness of the experimental data of Meerts and Dymanus, it seems likely that the difference between the dipole moments of OH and OD is not entirely due to vibrational effects. An explanation for this discrepancy may lie in the failure of the Born-Oppenheimer approximation, which has not been considered in the theoretical calculations nor in the interpretation of experimental data.

The vibrationally averaged dipole moments for the $A^2\Sigma^+$ state are $\mu(\text{OH}, v=0) = 1.875$ D, $\mu(\text{OH}, v=1) = 1.967$ D, $\mu(\text{OD}, v=0) = 1.861$ D, and $\mu(\text{OD}, v=1) = 1.934$ D. These are in good agreement with the previous theoretical results¹⁷ of $\mu(\text{OH}, v=0) = 1.89$ D, $\mu(\text{OH}, v=1) = 2.01$ D, $\mu(\text{OD}, v=0) = 1.87$ D, and $\mu(\text{OD}, v=1) = 1.96$ D. There are two experimental results for the $v=0$ level of OD: 1.72 ± 0.10 D by Weinstock and Zare,¹⁸ and 2.16 ± 0.08 D by Scarl and Dalby.¹⁹ Our value, even if we include a very conservative error estimate of 0.1 D, is

consistent with the value of Weinstock and Zare, but not with that of Scarl and Dalby.

The vibrationally averaged hyperfine constant eqQ for the $A^2\Sigma^+$ state of OD are 0.264 and 0.254 MHz for the $v=0$ and $v=1$ levels, respectively. These values are in excellent agreement with the previous CI results of 0.262 and 0.258 MHz obtained by Green,¹⁷ but not consistent with the experimental value of 0.09 ± 0.05 MHz obtained by Weinstock and Zare,¹⁸ for the $v=0$ level.

ACKNOWLEDGMENT

We gratefully acknowledge many helpful discussions with Dr. G. C. Lie. We are grateful to Dr. J. Hinze for making available his MCSCF program.

*This research was carried out under a Joint Study Agreement between Harvard College Observatory and the IBM Corporation. S. I. Chu was partially supported by the National Science Foundation.

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